CORRESPONDENCE/MEMORANDUM

State of Wisconsin

DATE: October 7, 2004 FILE REF: Air Toxics

TO: Caroline Garber

FROM: David Grande

SUBJECT: Atrazine in Wisconsin Air

Atrazine is one of the most widely used agricultural chemicals. Two main restrictions govern its use in Wisconsin. First, application of Atrazine is only legal between April 1 and July 31. Additionally, results showing its presence in groundwater have led to areas where its use is prohibited. Wisconsin counties with prohibition zones are shown in Figure 1 below. {This figure is from Department of Agriculture, Trade and Consumer Protection web pages during 1999. Their current web page has only county level maps. Calumet County now shares a prohibition zone with Manitowoc County. Otherwise, there have been no new counties added through 2004.}

Figure 1: Atrazine Prohibition in Wisconsin

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State level detailed summaries of agricultural chemical use are available from the National Agricultural Statistics Service (NASS). County level detail is not included in these NASS reports. Statistics include the quantity applied to how much acreage for each crop and chemical included in the survey. The data are extrapolated from voluntary surveys completed by individual farmers. Atrazine is primarily used on corn, with a much smaller consumption in some forestry applications (such as Christmas trees).

The NASS considers field corn separately from sweet corn. Field corn statistics are collected annually with other field crops, while sweet corn is included with other vegetable crops in a separate survey compiled every other year. Available sweet corn statistics have not been included, as they were found to contain less than 1% of the atrazine consumption in the years they were reported.

Atrazine consumption data for Wisconsin field corn is presented in the following table. This data was obtained from the NASS at http://usda.mannlib.cornell.edu/reports/nassr/other/pcu-bb.

Table 1: Estimated Atrazine Use in Wisconsin

Year	Acres Planted	Percent Applied	Acres Applied	Pounds Applied
1995	3,650,000	51%	1,861,500	1,887,000
1996	3,900,000	51%	1,989,000	1,474,000
1997	3,800,000	64%	2,432,000	1,940,000
1998	3,700,000	56%	2,072,000	1,789,000
1999	3,560,000	37%	1,317,200	1,054,000
2000	3,500,000	52%	1,820,000	1,424,000
2001	3,400,000	59%	2,006,000	1,811,000
2002	3,650,000	47%	1,715,500	1,537,000
2003	3,800,000	58%	2,204,000	1,708,000
2004	not yet available			

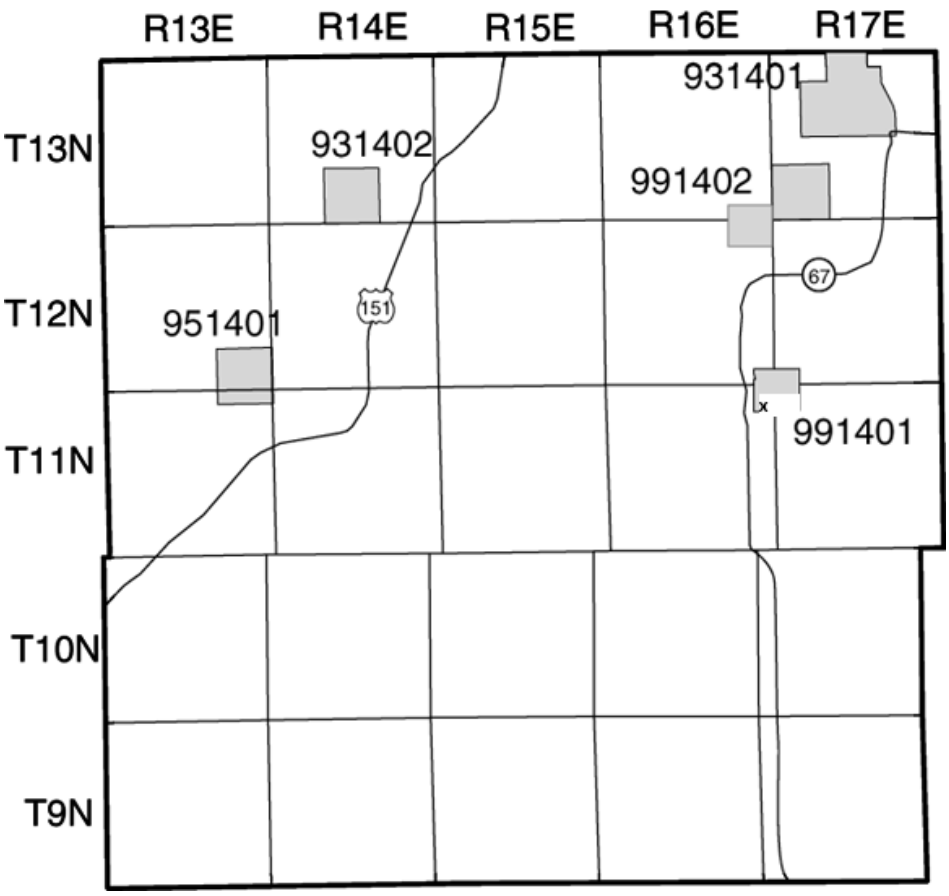
Little is known about volatilization and drift of agricultural chemicals, and their impact on local and regional air quality. How far agricultural chemicals may migrate from their point of origin is unknown, however studies have shown the presence of toxaphene in the Great Lakes even though the closest use of this chemical is on the cotton fields in the south. Health or environmental hazards which may be associated with these chemicals in air are not well characterized.

Atrazine sampling and analysis is included at the National Rural Toxic Trends Air Monitoring site located near Mayville, Wisconsin. The Mayville sampling site is located within an atrazine prohibition zone in Dodge County (zone number 991401). Figure 2 on the following page shows the prohibited areas in Dodge County (from DATCP web pages, September 2004) (approximate site location marked with an "x").

A total of 12 samples, partially on a 1-in-12 day and partially on a 1-in-6 day cycle, were attempted between 4/3/04 and 6/22/04. One sample failed to start and was submitted as a field blank (completeness of 91.7%). These results are the primary purpose of this memo.

The Wisconsin Urban Air Toxics Monitoring program also included Atrazine as an analytical parameter until budget shortfalls in 2004. Analysis is performed on the initial extract of polyurethane foam samples prior to fractionation for PCB analysis, using gas chromatography with a nitrogen specific detector. Note that PCB analysis on the Mayville samples was not conducted. While year-round analysis for this parameter was performed prior to 1997, the lack of detects before April and after August led to a spring and summer pattern of analysis since that time.

Figure 2: Dodge County Atrazine Prohibition Zones



Samples are generally collected over 3 days on a 1-in-12 day cycle between April and August or September. Several exceptions to this protocol exist, including the first Mayville sample, which was collected over a single 6-day period, and the single Trout Lake sample, which was collected over 5 weeks, with the sampler running 3 days per week. Winter sampling prior to 1998 was collected over two 3-day periods on a 1-in-12 day cycle.

This report includes all atrazine data collected from 1995 through 2004. Sites sampled at are Mayville (2004), Green Bay (GB) (1995 – 2003), Wisconsin Rapids (WR) (1997 – 2000), Sixteenth Street in Milwaukee (SS) (2000 – 2003), Madison East (ME) (2002 – 2003), and a single sample from Trout Lake (TL) in 2001. Note that Mayville is in an agricultural area and Trout Lake is a remote site, while the remaining sites are urban. Milwaukee and Vilas counties (Trout Lake) do not have prohibition areas. Dane county has the most extensive prohibition zones, covering the majority of the county.

Results

Atrazine was detected in 9 of 11 samples collected at the Mayville site in 2004 (a detection rate of 81.8%). Observed concentrations ranged from <0.09 to 2.13 ng/m^3, with an average of <0.73 ng/m^3 (0.86 ng/m^3 when non-detects are discounted). Tables 2 and 3 below present these results in summary and complete form.

Table 2: Mayville Atrazine Result Summary, 2004

Calculation	Average	Max	Min	RSD	Detects	Samples	Detection Rate
No non-detects	0.86	2.13	0.20	77.5%	9	11	81.8%
At detection	<0.73	2.13	<0.09	91.0%			

Table 3: Mayville Atrazine Results Complete, 2004

Date	Detect?	Ambient	Units	Date	Detect?	Ambient	Units
03-Apr-04	N	<0.09	ng/m3	**21-May-04**	N	<0.19	ng/m3
15-Apr-04	Y	1.48	ng/m3	**27-May-04**	Y	0.20	ng/m3
27-Apr-04	Y	1.49	ng/m3	**03-Jun-04**	Y	0.29	ng/m3
03-May-04	Y	0.64	ng/m3	**08-Jun-04**	Y	2.13	ng/m3
09-May-04	Y	0.50	ng/m3	**20-Jun-04**	Y	0.48	ng/m3
15-May-04	Y	0.55	ng/m3				

An additional 235 UATM samples collected between 1995 and 2003 have been analyzed for atrazine, of which 83 have contained detectable quantities (35.3% detection rate). Annual summaries of these results by site are presented in Tables 4 and 5 on the following page. Summary calculations for Table 4 include non-detects evaluated at the detection limit, while Table 5 discounts these values.

In addition to basic summary statistics, Table 4 shows the dates of sampling, with the number of sample days and percentage of the year during which samples were actually collected. Table 5 includes the number of detects and samples, along with the number of detects observed before 5/1 and after 7/1.

While the Mayville samples are not directly comparable to the remaining data because of protocol changes and non-concurrent sampling, some general observations can be made.

- Of a total of 92 detects, 74 (80.4%) have been obtained in May and June, with the remainder observed in April and July.

- A total of 8 results (3.2% of all samples) exceed 0.7 ng/m^3, of which 3 (37.5%) were observed at Mayville. These 3 results are the second through fourth highest values observed. All 8 results are examined in more detail later in this document

- The average value observed at Mayville (0.86 ng/m^3 excluding the two non-detects) is higher than any of the other sites.

- The 81.8% detection rate is the highest observed in our sampling (with the exception of the single detected quantity at Trout Lake, where an extended sampling period reduced the detection limit by a factor of about 5).

- The highest individual sample result (2.26 ng/m^3) was obtained at the Sixteenth Street monitoring site in Milwaukee, during 2001.

The first four observations are not especially surprising, as atrazine is used primarily between April and June and the Mayville site is located closest to areas where it may be used. However, many may be surprised at the prevalence of this chemical in urban air at any level, much less at a concentration greater than that observed in an agricultural area.

Table 4: Historic UATM Atrazine Results, 1995 – 2003

		non-detects at detection limit				Sampling Dates			Sample	percent
Site	Year	Average	Max	Min	RSD	Start	End	Days	Days	sampled
GB	1995	<0.21	0.62	<0.08	63.8%	1/9/95	1/2/96	358	93	25.5%
GB	1996	<0.20	0.60	<0.08	57.6%	1/4/96	12/27/96	358	93	25.4%
GB	1997	<0.20	0.52	<0.07	50.0%	1/6/97	9/21/97	258	60	16.4%
GB	1998	<0.31	0.65	<0.19	44.2%	4/23/98	8/23/98	122	30	8.2%
GB	1999	<0.22	0.27	<0.17	14.8%	4/18/99	8/18/99	122	33	9.0%
GB	2000	<0.35	1.36	<0.17	104.1%	4/15/00	7/19/00	95	27	7.4%
GB	2001	<0.37	1.24	<0.16	82.5%	4/19/01	8/31/01	134	33	9.0%
GB	2002	<0.29	0.64	<0.14	60.3%	4/26/02	8/2/02	98	27	7.4%
GB	2003	<0.28	0.61	<0.17	68.1%	5/3/03	7/28/03	86	24	6.6%
ME	2002	<0.18	0.26	<0.11	40.3%	6/25/02	7/21/02	26	9	2.5%
ME	2003	<0.24	0.45	<0.17	41.9%	4/21/03	7/26/03	96	24	6.6%
SS	2000	<0.36	1.34	<0.17	110.5%	4/14/00	7/31/00	108	24	6.6%
SS	2001	<0.52	2.26	<0.14	131.1%	4/19/01	7/27/01	99	27	7.4%
SS	2002	<0.28	0.51	<0.15	50.7%	4/26/02	8/2/02	98	27	7.4%
SS	2003	<0.23	0.35	<0.15	33.2%	5/3/03	7/28/03	86	24	6.6%
TL	2001		0.04			5/29/01	7/4/01	36	15	4.1%
WR	1997	<0.21	<0.23	<0.18	10.3%	7/9/97	9/21/97	74	21	5.8%
WR	1998	<0.29	0.84	<0.19	63.7%	4/24/98	8/23/98	121	33	9.0%
WR	1999	<0.28	0.51	<0.19	42.7%	4/18/99	8/19/99	123	36	9.9%
WR	2000	<0.24	0.49	<0.18	46.5%	4/12/00	6/25/00	74	18	4.9%

Table 5: Historic UATM Atrazine Results, 1995 - 2003

		Discounting non-detects				Detection Rates			detects	detects
Site	Year	Average	Max	Min	RSD	Detects	Samples	Rate	Pre-5/1	Post 7/1
GB	1995	0.47	0.62	0.23	36.4%	5	32	15.6%	0	0
GB	1996	0.35	0.49	0.21	32.2%	4	32	12.5%	0	4
GB	1997	0.27	0.52	0.16	37.5%	10	21	47.6%	1	0
GB	1998	0.49	0.65	0.34	32.1%	3	11	27.3%	0	0
GB	1999		0.27			1	11	9.1%	0	1
GB	2000	0.51	1.36	0.20	93.1%	5	10	50.0%	0	0
GB	2001	0.49	1.24	0.21	68.6%	8	13	61.5%	1	1
GB	2002	0.40	0.64	0.18	43.2%	6	11	54.5%	0	1
GB	2003	0.40	0.61	0.17	59.6%	4	9	44.4%	N/A	0
ME	2002		0.26			1	3	33.3%	N/A	0
ME	2003	0.29	0.45	0.17	42.4%	4	8	50.0%	0	0
SS	2000	0.67	1.34	0.33	86.1%	3	8	37.5%	1	0
SS	2001	0.81	2.26	0.21	102.6%	5	9	55.6%	1	0
SS	2002	0.37	0.51	0.20	33.0%	5	9	55.6%	0	0
SS	2003	0.29	0.35	0.24	19.9%	4	8	50.0%	N/A	1
TL	2001	0.04				1	1	100.0%	N/A	N/A
WR	1997	no detects				0	8	0.0%	N/A	0
WR	1998	0.39	0.84	0.20	66.5%	5	12	41.7%	0	0
WR	1999	0.33	0.51	0.20	37.7%	7	12	58.3%	2	1
WR	2000	0.38	0.49	0.28	37.9%	2	7	28.6%	1	N/A

Data Combinations

The agricultural statistics and monitoring results from both urban and rural sampling are combined in the following figures. Figure 3 shows a graphical representation of the comparison of atrazine consumption and the average number of detected samples per site for each year between 1995 and 2003. Figure 4 compares the average and maximum statewide air concentrations with consumption. Averages used are based on detected quantities only. In each case, atrazine use is in millions of pounds, and is relative to the secondary y-axis.

Figure 3: Atrazine Use and # Detects

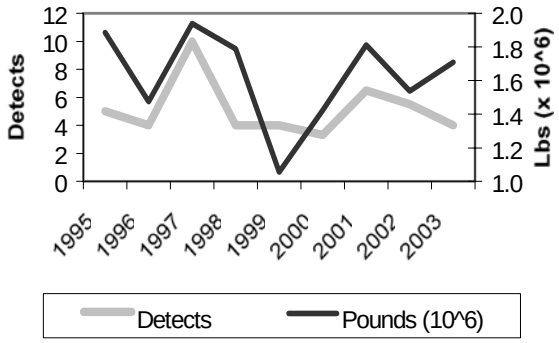
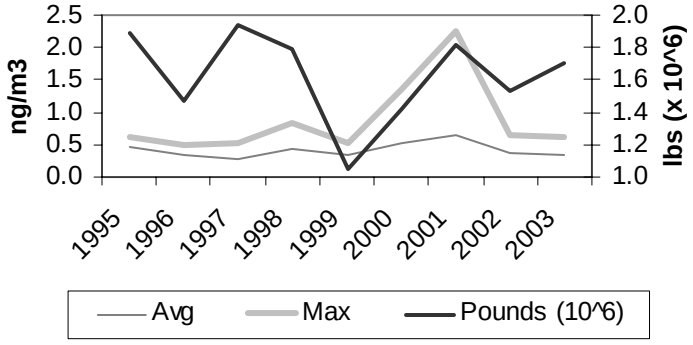


Figure 4: Atrazine Use and ng/m^3



These figures illustrate the likelihood that there is a direct relation between application of atrazine and it's presence in Wisconsin air. How direct a relationship, and how much is related to more regional use of the chemical can not be determined from the available data. Current detection limits and a lack of specific application data (ie: dates and locations of actual applications) do not allow a determination of how long after application atrazine remains present in ambient air, or how far the material may travel before deposition or chemical transformation.

Another set of data available is meteorological data, including wind speed, wind direction and temperature. Averaging these parameters over the extended sampling period (72 hours) required to achieve detection of this compound has difficulties. Winds tend to change during this time period, so it is rare to collect a sample which is influenced entirely from a single quadrant.

Nonetheless, some useful information may be obtained from evaluating atrazine concentrations in light of these parameters. The tables on the following page present the data from Mayville and from the 8 highest concentration samples. Note that the first Mayville sample was collected over the course of 6 days (a 144-hour sample).

Reported meteorological parameters include the overall vector mean averaged wind speed and wind direction, and the overall average temperature, as well as daily means. Temperature is in degrees Fahrenheit. Individual hourly average wind speeds of less than 2.5 mile per hour are considered calm conditions and have not been included in the vector mean averaging calculations.

Note that only two samples (Mayville, May 21, 2004 in Table 6 and Green Bay, May 6, 2000 in Table 7) show a variation in wind direction of less than 60 degrees, thus illustrating the difficulty in assigning importance to this parameter when evaluating these results.

Table 6: Meteorological Data for Mayville Sampling Days

Starting Date	Atrazine ng/m3	SUM			Day 1			Day 2			Day 3		
		WS	WD	T	WS	WD	T	WS	WD	T	WS	WD	T
03-Apr-04	<0.09	2.6	350	42.1	16.2	330	38.8	6.4	0	33.6	6.7	160	37.6
					4.2	210	51.1	8.5	120	48.7	8.9	330	43.0
15-Apr-04	1.48	6.3	160	59.0	11.8	170	57.5	7.8	190	65.9	7.4	80	53.8
27-Apr-04	1.49	12.3	220	55.7	5.3	290	38.8	20.6	200	63.1	15.7	230	65.2
03-May-04	0.64	4.8	200	48.6	1.9	170	40.2	8.2	240	54.7	7.4	170	50.9
09-May-04	0.50	3.6	140	59.7	3.6	130	60.3	3.3	220	60.2	7.3	120	58.7
15-May-04	0.55	5.3	180	54.9	2.4	60	46.5	8.9	170	53.3	10.0	210	65.0
21-May-04	<0.19	4.3	80	55.1	7.7	80	51.5	4.0	80	56.6	1.1	90	57.2
27-May-04	0.20	2.9	110	52.7	3.8	270	58.8	3.2	50	50.1	10.7	120	49.3
03-Jun-04	0.29	3.1	110	60.4	4.4	50	56.9	4.3	110	60.7	5.7	170	63.7
08-Jun-04	2.13	3.4	140	66.2	9.7	210	77.3	2.7	90	67.3	8.5	80	54.0
20-Jun-04	0.48	5.9	240	60.4	8.0	230	61.2	6.8	210	59.5	7.3	300	60.3

Table 7: Meteorological Data on Maximum Atrazine Sample Days

Site	Start Date	Atrazine ng/m3	SUM			Day 1			Day 2			Day 3		
			WS	WD	T	WS	WD	T	WS	WD	T	WS	WD	T
SS	01-May-01	2.26	3.7	210	65.2	8.7	210	70.3	7.1	200	68.6	4.8	10	56.8
MV	08-Jun-04	2.13	3.4	140	66.2	9.7	210	77.3	2.7	90	67.3	8.5	80	54.0
MV	27-Apr-04	1.49	12.3	220	55.7	5.3	290	38.8	20.6	200	63.1	15.7	230	65.2
MV	15-Apr-04	1.48	6.3	160	59.0	11.8	170	57.5	7.8	190	65.9	7.4	80	53.8
GB	06-May-00	1.36	10.4	225	72.0	10.4	200	72.0	10.0	220	74.0	12.9	250	70.0
SS	14-Apr-00	1.34	2.0	70	43.3	11.3	210	57.0	4.9	40	39.0	11.9	50	34.0
GB	30-Jun-01	1.24	3.1	330	66.3	8.9	290	80.0	11.5	350	60.0	8.4	140	59.0
WR	19-May-98	0.84	3.2	330	66.2	6.3	290	74.7	4.8	330	64.4	3.9	60	59.8

In spite of the scarcity of our data and the difficulties in relating the results to local or regional influences, our sampling shows that this chemical does consistently appear in Wisconsin's air. Further sampling will be useful in further evaluating trends and impacts.

Recommendations

Several factors may enhance our atrazine sampling program and yield more useful data.

1) Re-instate sampling at all current UATM semi-volatile organic compound sampling sites, including Mayville, Green Bay and Sixteenth Street in Milwaukee. Concurrent sampling at both urban and rural sites will provide a greater base for comparison.

2) Standardizing the sampling season to encompass the entire legal application timeframe will allow more direct comparison between different years. Recommend sampling between April 1 and July 31 each year.

3) Elevated concentrations may be relatively short term events. Recommend sampling on a 1 in 6 day cycle to capture as much data as possible.